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## 13. ABSTRACT (Maximum 200 words)

Electro-optic chromophores (FTC and CLD) were synthesized in bulk (kilogram) quantities and were distributed to the participants of this program project (Steier, Fetterman, Chen, and TACAN/IPITEK). They were also provided to other Department of Defense programs including to researchers at China Lake (Navy), Redstone Arsenal (Army), and Wright Paterson (Air Force Research Laboratory) and to various industrial programs (e.g., Lockheed Martin) participating in DoD research programs. FTC and CLD chromophores were systematically modified to improve their properties, including for lattice hardening to stabilize electro-optic activity for operation at elevated temperatures and photon flux levels. Over 100 variants of these chromophores were synthesized and were evaluated. Reaction yields were optimized by systematically variation of reaction conditions. New chromophores were also synthesized at the University of Washington including those involving incorporation of significantly improved chromophores. These new materials involve factors of 1.5-2.0 improvement over FTC and CLD chromophores in terms of electro-optic activity at telecommunication wavelengths. They also have proven more amenable to being processed into hardened material lattices and have exhibited significantly improved thermal and photochemical stability. The role of chromophore structure and the use of radical (and singlet oxygen) scavengers have been investigated. The results can be utilized to fabricate materials with significantly improved photochemical stability.

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# **Advanced Organic Electro-Optic Materials for Integrated Device Applications**

## **Final Report**

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### **Abstract**

Electro-optic chromophores (FTC and CLD) were synthesized in bulk (kilogram) quantities and were distributed to the participants of this program project (Steier, Fetterman, Chen, and TACAN/IPITEK). They were also provided to other Department of Defense programs including to researchers at China Lake (Navy), Redstone Arsenal (Army), and Wright Paterson (Air Force Research Laboratory) and to various industrial programs (e.g., Lockheed Martin) participating in DoD research programs.

FTC and CLD chromophores were systematically modified to improve their properties, including for lattice hardening to stabilize electro-optic activity for operation at elevated temperatures and photon flux levels. Over 100 variants of these chromophores were synthesized and were evaluated. Reaction yields were optimized by systematic variation of reaction conditions. New chromophores were also synthesized at the University of Washington including those involving incorporation of significantly improved chromophores. These new materials involve factors of 1.5-2.0 improvement over FTC and CLD chromophores in terms of electro-optic activity at telecommunication wavelengths. They also have proven more amenable to being processed into hardened material lattices and have exhibited significantly improved thermal and photochemical stability.

The role of chromophore structure and the use of radical (and singlet oxygen) scavengers have been investigated. The results can be utilized to fabricate materials with significantly improved photochemical stability.

### **Progress Report**

The use of the CLD chromophore for device fabrication and evaluation is discussed extensively in the accompanying Steier report and will not be reproduced here. The development of crosslinkable versions of the CLD chromophore is described in References 26 and 36. In these references, we also report the first systematic study of the photostability of polymeric electro-optic materials at telecommunication wavelengths. The dominant decomposition mechanism is shown to involve singlet oxygen. Maintenance of an argon rich atmosphere above polymeric electro-optic modulators results in dramatic improvement in the stability of electro-optic activity as is shown in the accompanying figure. Photostability is also enhanced by use of singlet oxygen scavengers and by lattice hardening (which reduces oxygen diffusion rates).

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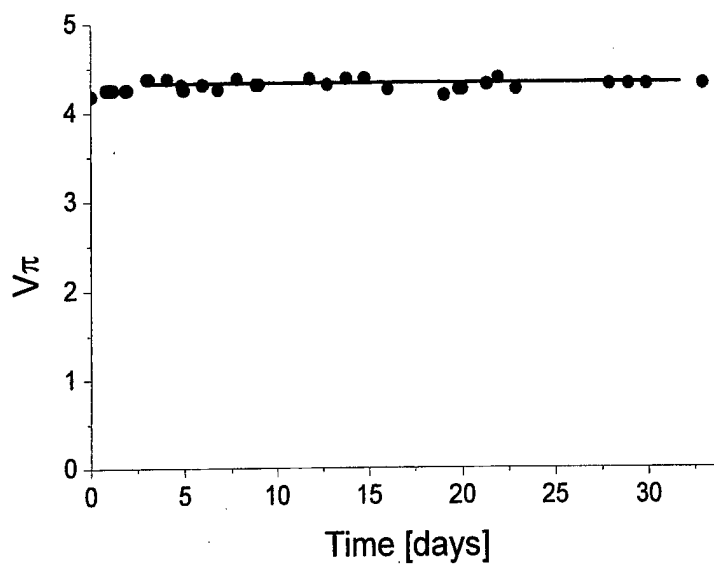


Figure 1. Drive voltage photostability recorded for 20 mW output power at 1.55 microns wavelength.

### Photo Stability of Different FTC Samples

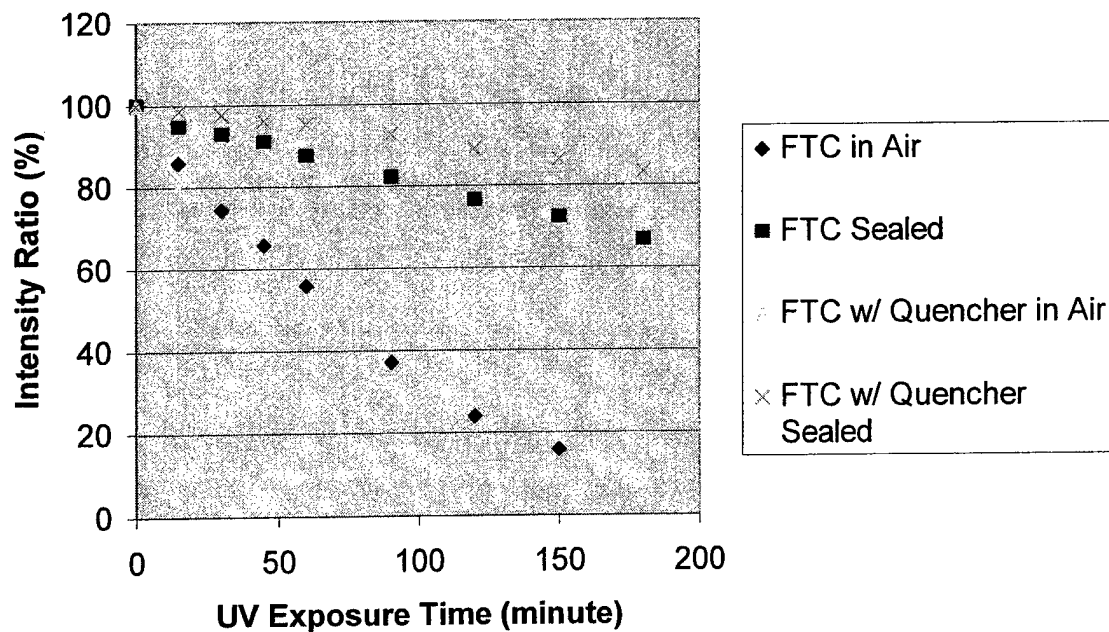


Figure 2. The effect of addition of quenchers on the photostability of FTC is shown. The measurements are for irradiation of a sample with a 400 watt lamp (directly into the interband

transition). The quencher results in some plasticization of the host lattice, which accounts for the acceleration of the photodegradation rate in the presence of air (excess oxygen).

Similar results have been realized for CLD-type chromophores in PMMA and APC host matrices. Moreover, we have examined a wide range of quenchers and have found substantial variability for different quenchers. It is clear that significant improvement in photostability can be achieved by exploiting the our finding during the past contract period.

## References

1. A. Chen, V. Chuyanov, F. I. Marti-Carrera, S. M. Garner, W. H. Steier, J. Chen, S. S. Sun, and L. R. Dalton, "Vertically Tapered Polymer Waveguide Mode Size Transformer for Improved Fiber Coupling," *Opt. Eng.*, **39**, 1507-16 (2000).
2. L. Sun, J.-H. Kim, C.-H. Jang, J. J. Maki, D. An, Q. Zhou, X. Lu, J. M. Taboada, R. T. Chen, S. Tang, H. Zhang, W. H. Steier, A. S. Ren, and L. R. Dalton, "Beam Deflection With Electro-Optic Polymer Waveguide Prism Array," *Proc. SPIE*, **3950**, 98-107 (2000).
3. J. S. Grote, J. S. Zetts, J. P. Drummond, R. L. Nelson, F. K. Hopkins, C. H. Zhang, L. R. Dalton, and W. H. Steier, "Effect of Dielectric Constant on Modulation Voltage for Nonlinear Optic Polymer-Based Optoelectronic Devices," *Proc. SPIE*, **3950**, 108-116 (2000).
4. C. Wang and L. R. Dalton, "A Facile Synthesis of Thienylmethylphosphonates: Direct Conversion From Thiophenes," *Tetrahedron Lett.*, **41**, 617-20 (2000).
5. I. Liakatas, C. Cai, M. Bosch, M. Jager, Ch. Bosshard, P. Gunter, C. Zhang, and L. R. Dalton, "Importance of Intermolecular Interactions on the Nonlinear Optical Properties of Poled Polymers," *Appl. Phys. Lett.*, **76**, 1368-70 (2000).
6. D. An, Z. Shi, L. Sun, J. M. Taboada, Q. Zhou, X. Lu, R. T. Chen, S. Tang, H. Zhang, W. H. Steier, A. Ren, and L. R. Dalton, "Polymeric Electro-Optic Modulator Based on 1x2 Y-Fed Directional Coupler," *Appl. Phys. Lett.*, **76**, 1972-4 (2000).
7. C. Zhang, A. W. Harper, D. S. Spells, and L. R. Dalton, "A Facile Synthesis of 5-N,N-Bis(2-Hydroxyethyl)amino-2-Thiophenecarboxaldehyde," *Synth. Commun.*, **30**(8), 1359-64 (2000).
8. C. Wang, C. Zhang, P. Wang, P. Zhu, C. Ye, and L. R. Dalton, "High Tg Donor-Embedded Polyimides for Second-Order Nonlinear Optical Applications," *Polymer*, **41**, 2583-90 (2000).
9. Y. Shi, C. Zhang, H. Zhang, J. H. Bechtel, L. R. Dalton, B. H. Robinson, and W. H. Steier, "Low (Sub-1 Volt) Halfwave Voltage Polymeric Electrooptic Modulators Achieved by Control of Chromophore Shape," *Science*, **288**, 119-122 (2000).
10. L. R. Dalton, "Polymeric Electro-Optic Materials: Optimization of Electro-Optic Activity, Minimization of Optical Loss, and Fine-Tuning of Device Performance," *Opt. Eng.*, **39**, 589-95 (2000).
11. S. S. Lee, S. M. Garner, V. Chuyanov, H. Zhang, W. H. Steier, F. Wang, L. R. Dalton, A.H. Udupa, and H. R. Fetterman, "Optical Intensity Modulator Based on a Novel Electrooptic Polymer Incorporating a High  $\mu\beta$  Chromophore," *IEEE Journal of Quantum Electronics*, **36**, 527-32 (2000).
12. B. H. Robinson and L. R. Dalton, "Monte Carlo Statistical Mechanical Simulations of the Competition of Intermolecular Electrostatic and Poling Field Interactions in Defining Macroscopic Electro-Optic Activity for Organic Chromophore/Polymer Materials," *J. Phys. Chem.*, **104**, 4785-4795 (2000).
13. D. H. Chang, H. Erlig, M. C. Oh, C. Zhang, W. H. Steier, L. R. Dalton, and H. R. Fetterman, "Time Stretching of 102 GHz Millimeter Waves Using a Novel 1.55  $\mu\text{m}$  Polymer Electrooptic Modulator," *IEEE Photonics Technology Letters*, **12**, 537-9 (2000).
14. D. An, S. Tang, Z. Shi, L. Sun, J. M. Taboada, Q. Zhou, X. Lu, R. T. Chen, H. Zhang, W. H. Steier, A. Ren, and L. R. Dalton, "1x2 Y-Fed Directional Coupler Modulator Based on Electro-Optic Polymer," *Proc. SPIE*, **3950**, 90-7 (2000).
15. Y. Shi, W. Lin, D. J. Olson, J. H. Bechtel, H. Zhang, W. H. Steier, C. Zhang, and L. R. Dalton, "Electro-Optic Polymer Modulators with 0.8 V Half-Wave Voltage," *Appl. Phys. Lett.*, **77**, 1-3 (2000).
16. M.-C. Oh, H. Zhang, A. Szep, V. Chuyanov, W. H. Steier, C. Zhang, L. R. Dalton, H. Erlig, B. Tsap, and H. R. Fetterman, "Practical Electro-Optic Polymer Modulators for 1.55  $\mu\text{m}$  Wavelength Using Phenyltetraene Bridged Chromophores in Polycarbonate," *Appl. Phys. Lett.*, **76**, 3525-7 (2000).

17. C. Zhang, M. Lee, A. Winkleman, H. Northcroft, C. Lindsey, A. K. Y. Jen, T. Londergan, W. H. Steier, and L. R. Dalton, "Realization of Polymeric Electro-Optic Modulators With Less Than One Volt Drive Voltage Requirement," Materials Research Society Symposium Proceedings, Vol. 598, Electrical, Optical and Magnetic Properties of Organic Solid State Materials (Materials Research Society, Pittsburgh, 2000) pp.BB4.2.1-12.
18. J. G. Grote, J. P. Drummond, J. S. Zetts, R. L. Nelson, F. K. Hopkins, C. Zhang, L. R. Dalton, and W. H. Steier, "Enhanced Electrooptic Activity of NLO Polymers Via the Use of Conductive Polymers," Materials Research Society Symposium Proceedings, Vol. 597, Thin Films for Optical Waveguide Devices (Materials Research Society, Pittsburgh, 2000) pp. 109-115.
19. A. Yacoubian, V. Chuyanov, S. M. Garner, W. H. Steier, A. S. Ren, and L. R. Dalton, "EO Polymer-Based Integrated-Optical Acoustic Spectrum Analyzer," IEEE J. Sel. Topics in Quantum Electronics, **6**, 810-6 (2000).
20. L. R. Dalton, B. H. Robinson, and W. H. Steier, "Production of High Bandwidth Polymeric Electro-Optic Modulators with  $V_{\pi}$  Voltages of Less Than 1 Volt," Mol. Cryst. Liq. Cryst.: Nonlin. Opt., **25**, 23-34 (2000).
21. H. R. Fetterman, D. H. Chang, H. Erlig, M. Oh, C. H. Zhang, W. H. Steier, and L. R. Dalton, "Photonic Time-Stretching of 102 GHz Millimeter Waves Using 1.55  $\mu\text{m}$  Polymer Electro-Optic Modulator," Proc. SPIE, **4114**, 44-57 (2000).
22. J. H. Bechtel, Y. Shi, H. Zhang, W. H. Steier, C. H. Zhang, and L. R. Dalton, "Low-Driving-Voltage Electro-Optic Polymer Modulators for Advanced Photonic Applications," Proc. SPIE, **4114**, 58-64 (2000).
23. J. S. Grote, J. S. Zetts, C. H. Zhang, R. L. Nelson, L. R. Dalton, F. K. Hopkins, and W. H. Steier, "Conductive Cladding Layers for Electrode Poled Nonlinear Optic Polymer Electro-Optics," Proc. SPIE, **4114**, 101-109 (2000).
24. L. R. Dalton, B. Robinson, W. H. Steier, C. H. Zhang, and G. Todorova, "Systematic Optimization of Polymeric Electro-Optic Materials," Proc. SPIE, **4114**, 65-76 (2001).
25. C. H. Zhang, G. Todorova, C. Wang, T. Londergan, and L. R. Dalton, "Synthesis of New Second Order Nonlinear Optical Chromophores: Implementing Lessons Learned from Theory and Experiment," Proc. SPIE, **4114**, 77-87 (2000).
26. C. Zhang, C. Wang, L. R. Dalton, H. Zhang, and W. H. Steier, "Progress Toward Device-Quality Second-Order Nonlinear Optical Materials. 4. A Tri-Link High  $\mu\text{B}$  NLO Chromophore in Thermoset Polyurethane: A "Guest-Host" Approach to Larger Electro-Optic Coefficients," Macromolecules, **34**, 253-61 (2001).
27. C. Zhang, C. Wang, J. Yang, L. R. Dalton, G. Sun, H. Zhang, and W. H. Steier, "Electric-Poling and Relaxation of Thermoset Polyurethane Second-Order Nonlinear Optical Materials: The Role of Cross-Linking and Monomer Rigidity," Macromolecules, **34**, 235-43 (2001).
28. H. Ma, B. Chen, S. Takafumi, L. R. Dalton, and A. K. Y. Jen, "Highly Efficient and Thermally Stable Nonlinear Optical Dendrimer for Electro-Optics," J. Am. Chem. Soc., **123** (5), 986-7 (2001).
29. C. Wang, C. Zhang, C. Zhou, M. Chen, and L. R. Dalton, "Urethane-Urea Copolymers Containing Siloxane Linkages: Enhanced Temporal Stability and Low Optical Loss for Second-Order Nonlinear Optical Applications," Macromolecules, **34**, 2359-63 (2001).
30. J. N. Woodford, C. H. Wang, C. Zhang, and L. R. Dalton, "Resonant and Nonresonant Hyper-Rayleigh Scattering of Charge-Transfer Chromophores," J. Appl. Phys., **89**, 4209-17 (2001).
31. H. Zhang, M.-C. Oh, A. Szep, W. H. Steier, C. Zhang, L. R. Dalton, H. Erlig, Y. Chang, D. H. Chang, and H. R. Fetterman, "Push Pull Electro-Optic Polymer Modulators with Low Half-wave Voltage and Low Loss at Both 1310 and 1550 nm," Appl. Phys. Lett., **78**, 3136-8 (2001).
32. L. R. Dalton, "Nonlinear Optical Polymeric Materials: From Chromophore Design to Commercial Applications," in Advances in Polymer Science, Vol 158 (Springer-Verlag, Heidelberg, 2001).
33. L. R. Dalton, "Electro-Optical Applications," in Encyclopedia of Polymer Science and Technology, (J. Kroschwitz, ed.) John Wiley & Sons, New York, 2000.
34. Y. V. Pereverev, O. V. Prezhdo, and L. R. Dalton, "Mean Field Theory of Accentric Order of Dipolar Chromophores in Polymeric Electro-Optic Materials. Chromophores with Displaced Dipoles," Chem. Phys. Lett., **340**, 328-35 (2001).
35. L. Sun, J. Kim, C. Jang, D. An, X. Lu, Q. Zhou, J. M. Taboada, R. T. Chen, J. J. Maki, S. Tang, H. Zhang, W. H. Steier, C. Zhang, and L. R. Dalton, "Polymeric Waveguide Prism Based Electro-Optic Beam Deflector," Opt. Eng., **40**, 1217-22 (2001).

36. C. Zhang, L. R. Dalton, M.-C. Oh, H. Zhang, and W. H. Steier, "Low  $V_{\pi}$  Electrooptic Modulators from CLD-1: Chromophore Design and Synthesis, Materials Processing, and Characterization," Chem. Mater., **13**, 3043-50 (2001).
37. B. H. Robinson and L. R. Dalton, "Defining Performance Limits for Polymeric EO Modulators," Proc SPIE, **4279**, 1-9 (2001).
38. J. H. Kim, L. Sun, C.-H. Jang, D. An, J. M. Taboada, Q. Zhou, X. Lu, R. T. Chen, X. Han, S. Tang, H. Zhang, W. H. Steier, A. Ren, and L. R. Dalton, "Polymeric Waveguide Beam Deflector for Electro-Optic Switching," Proc SPIE, **4279**, 37-44 (2001).
39. C. Zhang, A. W. Harper, and L. R. Dalton, "Formylation of Diethyl-2-Thienylmethyl-phosphonate for One-Pot Synthesis of Aminothienostilbene Carboxaldehyde," Synth. Commun., **31**(9), 1361-5 (2001).
40. L. R. Dalton, "Realization of Sub 1 Volt Polymeric EO Modulators Through Systematic Definition of Material Structure/Function Relationships," Synthetic Metals, **124/1**, 3-7 (2001).